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The Mass Spectrometer in Organic Chemistry

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Although mass spectrometry dates back to 1910, to the work of Thomson, Aston, Bainbridge, and Dempster, it was about 1940 that the mass spectrometer was put to work as an analytical tool for the chemists. From the early analyses of simple gaseous mixtures, mass spectrometry has expanded into nearly every branch of chemistry. This survey can only touch upon some typical applications to illustrate the usefulness of this powerful tool. The fundamentals in instrumentation and application in many aspects of mass spectrometry are thoroughly dealt with in two recent books by Barnard (1), and Ewald and Hintenberger (2), and in comprehensive chapters written by Stewart (3) and Washburn (4), as well as in numerous other works.

A mass spectrometer may be described briefly as an instrument in which gaseous molecules at low pressure are fragmented and ionized by a stream of electrons. The ions are sorted magnetically according to their mass-to-charge ratio, and their relative abundances are measured electrically, usually appearing as peaks on a recorder chart as the spectrum is scanned over the mass range of interest.

As an illustration of the fragmentation and ionization processes, acetone yields ions of various masses. Some of the acetone molecules simply lose an electron to form $CH_3COCH_3^+$ ions of mass 58. Others lose an electron and also fragment to form CH_3CO^+ ions of mass 43. Among the other ionized fragments are $CH_3COCH_2^+$, CH_3COCH^+, CH_3^+, CO^+, C^+, and H^+, some of which are present in only minute amounts. The usefulness of a mass spectrum for certain structural interpretations becomes apparent when one considers that the ions of a specific mass can arise only from combinations of atoms whose total masses equal the mass of that ion. An ion of mass 43, for instance, can be attributed only to CH_3CO^+, $C_3H_7^+$, or possibly $CHNO^+$.

The mass spectrum of a particular compound is unlike that of any other, and, under proper instrumental conditions, the magnitude of each peak in its spectrum is a linear function of the pressure of the compound in the spectrometer. When a mixture of two or more compounds is admitted, the spectrum of each one is added to the spectra of the others. These facts form the basis of qualitative and quantitative analyses by mass spectrometry.

Among the first users of the mass spectrometer as an analytical tool were those in the petroleum industry, where other physical or chemical methods of analysis of hydrocarbon mixtures left much to be desired. The subject of quantitative analysis of multicomponent mix-

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tures of hydrocarbons and other gases is discussed in detail by Hipple (5); by Washburn, Wiley, and Rock (6); and by Washburn, Wiley, Rock, and Berry (7). The superiority of the mass spectrometer over volumetric methods in the analysis of hydrocarbons has been demonstrated by Shepherd (8). Although only the lighter hydrocarbons have sufficient vapor pressure at room temperature to be analyzed by the mass spectrometer, O'Neal and Wier (9) developed instrumental improvements for volatilizing hydrocarbons up to C_{40}, and they extended the effective resolution up to mass 600.

In the mass spectrometric analysis of gasoline, Brown (10) has developed a method in which the compound types (paraffins; cycloparaffins and monoolefins; cycloolefins, diolefins and acetylenes; and aromatics) rather than specific compounds in the mixture are determined quantitatively.

Today, the analytical mass spectrometer is widely used and is almost commonplace throughout the petroleum industry, performing not only routine plant control analyses, but also playing an important rôle in research and development work. It was logical that a tool as useful as this would quickly find many applications outside the hydrocarbon field.

In making qualitative identifications, it is desirable to have available a large reference file of mass spectra of pure compounds. Rock (11) has published a thorough discussion of qualitative analyses from mass spectra, and has included a table of mass spectra of some 280 compounds, many of which are not hydrocarbons. The American Petroleum Institute has made available tabulated mass spectra of nearly a thousand compounds, including oxygenated, halogenated, and sulfur compounds, as well as inorganic gases and vapors. The mass spectra of over 700 compounds have been tabulated on Keysort punch cards for easy sorting and quick comparison with spectra of unknown materials. The cards have been made available by the Consolidated Engineering Company, of Pasadena, California.

An approach has been made by Kinney and Cook (12) to the identification of certain compounds for which reference spectra are lacking. They found it possible to identify, from correlations, the alkyl substituents in a thiophene homolog in the molecular-weight range from 126 to 154, or in a mono- or disubstituted benzene in the range from 120 to 148. Undoubtedly, correlation studies will be made for other classes of compounds, making it possible to obtain more information from the mass spectrum of an unknown material than now appears possible.

Frequently, mass spectrometry, infrared absorption spectrometry, and Raman spectrometry are all brought to bear upon an analytical or a chemical structure problem. Information is learned which could not be gained by any one of these alone, for mass spectrometry yields information different from that provided by the other two, with little overlap. Coggeshall (13) has presented a general and fundamental discussion of the usefulness of these fields in molecular spectroscopy, particularly as they pertain to the determination of functional groups.

A specific example of the combined use of mass spectrometry and infrared spectrometry is a method for the analysis of C_1 to C_4 paraffin and monoolefin hydrocarbons, as described by O'Neal (14). Mass spectrometric data provide the basis for simple total pressure computations and analytical data for the determination of most components. The split between *cis* and *trans* 2-butene, which is difficult to achieve by mass spectrometry, is readily accomplished by infrared spectrometry.

While it is not feasible to analyze directly complex organic materials such as resins, enamels, and rubber, Zemany (15) has shown how the mass spectro-

metric analysis of the pyrolysis products from these and other complex materials aids in the identification of the original material.

In the course of an analysis for a trace amount of an impurity, sometimes the impurity is masked by the principal compound. Honig (16) has demonstrated how one may intentionally change the ionizing conditions so that the lighter impurity is preferentially ionized, and therefore one may analyze certain mixtures that are ordinarily resolved with difficulty. This approach is particularly applicable for detecting nondeuterated compounds in the presence of deuterated hydrocarbons.

Because of its ability to analyze very small samples, the mass spectrometer has been successfully used for the analysis of solvent vapors in the air. Happ, Stewart, and Brockmyre (17) have described methods of determining solvent vapors that are present in air samples at the level of parts per million. Many components of a typical smog have been identified by Shepherd, Rock, Howard, and Stormes (18), who extended the range of detection to levels far lower than parts per million. By using special condensation techniques, Newton (19) has analyzed for traces of either condensable or noncondensable material in the presence of the other. The analysis of water contaminated with volatile hydrocarbons down to ten parts per billion has recently been accomplished by Melpolder, Warfield, and Headington (20).

In the measurement of vapor pressures of hydrocarbons below a few millimeters by conventional methods, it is necessary to use materials of extremely high purity. Tickner and Lossing (21) used a mass spectrometer to measure the partial pressure of a particular hydrocarbon in the presence of impurities which also exerted appreciable pressures.

The wide use of stable isotope concentrates for the tagging of molecules, atoms, and functional groups in molecules is well known, particularly in the fields of biochemistry where it is desired to follow the fate of a molecule in a living specimen. The mass spectrometer is used for analyzing the products of an experiment in which tagged stable atoms are used. Very small differences in isotopic ratios between two samples are most reliably measured on specialized isotope ratio mass spectrometers of the type developed by Nier (22).

The isotope dilution method of analysis, as described by Rittenberg and Foster (23), has been extended by Grosse, Hinden, and Kirschenbaum (24) to the determination of carbon, nitrogen, and oxygen in organic compounds. The carbon content is determined, for example, by adding to a weighed amount of the sample, a weighed amount of a compound containing a known enrichment in C^{13}. Some of the carbon dioxide that is liberated from ignition of the mixture is assayed by the mass spectrometer, and from the ratio of C^{12}:C^{13} the carbon content of the sample can be calculated.

The determination of heavy water by the mass spectrometer presents certain difficulties which have been minimized by special techniques described by Thomas (25), and by Washburn, Berry, and Hall (26).

The examples given here are typical of the many applications of mass spectrometry to organic chemistry. Comprehensive reviews of this subject by Shepherd and Hipple (27), by Dibeler and Hipple (28), and by Dibeler (29) cover many other uses that chemists have found for the modern mass spectrometer.

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New Eastman Organic Chemicals

6982	(2,2′-Biindan)-1,1′,3,3′-tetrone MP 315° dec.	10 g.	$2.10
	$COC_6H_4COCHCHCOC_6H_4CO$ . . . MW 290.26	25 g.	4.50
6183	2,2′-Biquinoline	½ g.	5.15
	$CH{:}CHC_6H_4N{:}CC{:}NC_6H_4CH{:}CH$ . . . MW 256.29	1 g.	9.75
P 6957	1,2,4-Butanetriol (Pract.) BP 150-152°/1 mm.	500 g.	2.90
	$CH_2OHCHOHCH_2CH_2OH$ . . . MW 106.12	1 kg.	5.30
1047	N,N′-Diethylcarbanilide MP 72-74°	25 g.	2.65
	$C_6H_5N(C_2H_5)CON(C_2H_5)C_6H_5$ . . . MW 268.35	100 g.	9.00
6979	2,2-Dimethylbutane BP 50-51°	500 g.	1.25
	$CH_3C(CH_3)_2CH_2CH_3$ . . . MW 86.17	2 kg.	3.40
6969	3,3′-Dimethyl-1,1′-diphenyl-(4,4′-bi-2-pyrazoline)-5,5′-dione	5 g.	2.00
	$CON(C_6H_5)N{:}C(CH_3)CHCHC(CH_3){:}NN(C_6H_5)CO$ . . . MW 346.38	10 g.	3.50
P 6958	2-Heptadecanone (Pract.) MP 40-44°	100 g.	1.60
	$CH_3CO(CH_2)_{14}CH_3$ . . . MW 254.44	500 g.	6.00
6981	Methyl m-Chlorobenzoate MP 18-19°	25 g.	2.75
	$ClC_6H_4COOCH_3$ . . . MW 170.59	100 g.	9.50

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